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CONTACT ISOMERIZATION OF AN ACETYLENE HYDROCARBON
WITH THE TRIPLE BOND IN THE CENTRAL POSITION

R. Ya. Levina, Ye. A. Viktorova, P. A. Akishin
Presented by Academician A. N. Nesmeyanov 18 February 1950
Submitted 30 December 1949

/Levina, Viktorova, and Akishin are engaged in work on the synthesis of olefins having a double bond located in the central part of the carbon chain. Such hydrocarbons can be prepared from dienes, and this actually has been done by Levina and her collaborators (cf. Zh. Obshchey Khimii, Vol XX, No 3, p 419, 1950). Hydrocarbons of this type have good antiknock properties. Kh. I. Areshidze (Izvestiya Akademii Nauk, Otdeleniye Khimicheskikh Nauk, No 3, pp 178-84, 1950) mentions the connection between work done by Levina's group and practical applications in the isomerization of olefin hydrocarbons contained in cracking gasoline/.

Two preceding reports (1) by Levina and her collaborators demonstrated that alpha- and beta-acetylene hydrocarbons (for example, pentyne-1, hexyne-1, and hexyne-2) underwent complete conversion in two directions as a result of contact with chromic oxide on aluminum oxide at 250 degrees centigrade; either the triple bond was transferred to the central position in the carbon chain or else two double conjugate bonds were formed. These reactions are formulated in the equations below:

$$CH_3CH_2CH_2C \equiv \begin{array}{l} \nearrow CH_3CH_2C \equiv CCH_3 \\ \searrow CH_3CH = CH-CH \equiv CH_2 \end{array}$$

$$CH_3CH_2CH_2CH_2C \equiv CH \begin{array}{l} \nearrow CH_3CH_2CH_2C \equiv CCH_3 \\ \searrow CH_3CH = CH-CH \equiv CH_3 \end{array}$$

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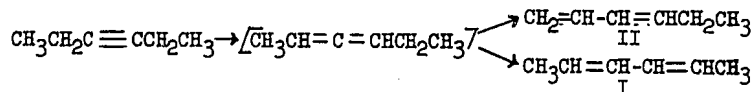| STATE	X	NAVY	X	NSRB		DISTRIBUTION							
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This report centered on the contact isomerization of hexyne-3 (a gamma-acetylenic hydrocarbon) under the same conditions as for the above reactions, and the researchers were able to deduce that only one type of conversion occurred: the triple bond was converted into two compounds, both with two conjugate bonds, as shown by the expression:

$$CH_3CH_2C \equiv CCH_2CH_3 \rightarrow [CH_3CH=C=CHCH_2CH_3] \begin{cases} CH_2=CH-CH=CHCH_2CH_3 \quad \text{II} \\ CH_3CH=CH-CH=CHCH_3 \quad \text{I} \end{cases}$$

Investigation of the spectra of combined light scattering showed that about 49 percent of the original hexyne-3 remained, and that about 33 percent of hexadiene-2, 4 and approximately 17-18 percent of hexadiene-1,3 were contained in the catalyzate. (A dispersion frequency of 1644 cm^{-1} established the probability of the latter product being hexadiene-1,3, this frequency being most likely produced by a diene of the type $CH_2=CH-CH=CH-$.)

The presence of hexadiene-2,4 in the catalyzate was shown also by the preparation of an adduct with maleic anhydride. In view of the fact that hexyne-1 and hexyne-2 were not present in the catalyzate, the triple bond was not moved from the middle position to the end of the carbon chain as was the case with pentyne-2 and hexyne-2 (1).

Therefore, hexyne-3 which has the least amount of free energy in the series including hexyne-1 and hexyne-2 (to judge from the magnitudes of the free energies required to form butyne-1 and butyne-2 -- 48.5 and 44.7 kilocalories/mole, respectively; and also to form pentyne-1 and pentyne-2 -- 50.2 and 46.4 kilocalories/mole (2), respectively, and still undergoes catalytic isomerization into hydrocarbons of the conjugated diene type.

SOURCES

1. R. Ya. Levina, Ye. A. Viktorova, and V. I. Eykhfel'd, Zhur. Ob. Khim., XIX, 305, 1949; R. Ya. Levina, Vestn. Mosk. Gos. U., No 10, 123, 1948

2. A. A. Vvedenskiy, Thermodynamic Calculations for Fuel Industry Processes, 435, 1949

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